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AGING IN THIN METALLIC FILMS

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Low magnetostriction NiFe and NiFe based ternary films 220Å to 340Å thick were prepared by thermal evaporation and bias sputtering. A few evaporated films were sputter etched. The films were aged in air with a magnetic bias in the plane of the film and perpendicular or parallel to the easy axis. Changes in uniaxial anisotropy field, coercive force and magnetostriction were measured as a function of time at temperatures of 100°C to 225°C. Films aged below 125°C in easy axis fields had an activation energy of 0.75ev in the case of evaporated NiFe while no change was observed in the → next page

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case of sputtered or sputter etched NiFe or for a ternary Ni-Fe-Au. All films responded to temperatures above 125°C with activation energies of 1.3 to 2.4 ev. The rate of response was 50 to 1000 times greater in evaporated NiFe than in the other films. All films stored at 150°C in a hard axis field showed a large decrease in anisotropy field. The rate of change was dependent on deposition conditions and annealing temperature. Sputter etching was capable of reorienting the anisotropy axis.

SUMMARY

This report gives measurements of changes in the magnetic properties of thin films due to oxidation. Evaporated NiFe films undergo changes in magnetic properties from oxidation 50 to 1000 times more rapidly than evaporated Ni-Fe-Au, sputter etched evaporated Ni-Fe or bias sputtered Ni-Fe films. A change in anisotropy occurs in all films aged with the magnetization other than parallel to the easy axis. The change can be reduced but not eliminated by a high temperature vacuum anneal of the film with a bias field parallel to the easy axis. Ni-Fe-Au films have lower dispersion and skew than evaporated NiFe but also have lower magnetoresistance as do bias sputtered Ni-Fe films. Evaporated Ni-Fe films when sputter etched retain their value of magnetoresistance. Sputter etching allows a rapid rotation of the anisotropy axis into coincidence with an applied field.

Information in this report can be used to predict changes in magnetic properties that may occur if the films are subjected to high temperatures in device fabrication or final use.

P. R. Wessel

P. R. WESSEL
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PREFACE

This work was undertaken to determine the aging characteristics of thin magnetic films which will be used in the cross tie memory.

The authors wish to thank John W. McCorkle for constructive criticisms during preparation of the report, for design and installation of the r.f. bias sputter matching network used in the course of this work and for verifying the calibration of instrumentation associated with the evaporator and the film characterizing equipment.

CONTENTS

Introduction

Frequently changes in the magnetic properties of thin films are due to either magnetic annealing or oxidation. Magnetic annealing can cause an increase or decrease in anisotropy field (H_k) depending on whether the bias field is parallel or perpendicular to the easy axis of the film. Annealing effects are believed to be due to iron pair ordering caused by vacancy migration which occurs in two stages. For the first stage of excess vacancy conditions, the activation energy and frequency factor are 0.85ev and 10^7 sec^{-1}. For the final stage of equilibrium vacancy conditions the values are 2.2ev and 10^{14} sec^{-1}.[1] Films that have not been stabilized by a high temperature anneal with an easy axis bias have additional activation energies.[2]

A marked increase in the coercive force (H_c) of films heated in air is due to oxidation since films heated in a vacuum or protected by an overcoating of SiO, Al_2O_3, or Si_3N_4 do not show a change in H_c.[3] Where overcoating is not practical or where films have to be processed at elevated temperatures, the oxidation rate of uncoated films is of interest.

Magnetostriction, defined $\eta = \Delta H_k/S$ where ΔH_k is a strain induced change in anisotropy and S the strain, is the film parameter most sensitive to oxidation. Oxidation that produces a 0.1 Oe change in H_c will typically change η by $6 \cdot 10^3$, equivalent to a 3 Oe change in H_k at $5 \cdot 10^{-4}$ strain. Generally magnetostriction is an indicator of film composition. Compositions were adjusted for low values of η in the films of interest here. Strain sensitivity can occur as a result of inadequate compositional control during deposition or compositional modification following deposition.

The films used for the experiments were 200Å to 340Å thick. NiFe films were prepared by thermal evaporation and by bias sputtering. A few of the evaporated films were treated by sputter etching in Argon. Several ternary films were prepared by addition of the third component to a Ni-Fe melt adjusted in Ni to Fe ratio for minimum magnetostriction.

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1. Takayasu, M. et al, IEEE Trans. Magn. MAG-10, 552 (1974).
2. Fujii, T. et al, IEEE Trans. Magn. MAG-4, 515 (1968).
3. Gangulee, A. et al, IEEE Trans. Magn. MAG-10, 848 (1974).

The films were aged following initial measurement of H_k, H_c and η and the measurements were repeated after the aging. In some cases additional quantities were monitored. The observations are reported with a discussion following.

Experimental

The evaporated films were made in a 10^{-6} torr vacuum by vapor deposition onto substrates of Corning 7059 or 0211 glass heated to 320°C. A 5-gram source in a resistance heated crucible provided a deposition rate of 1000Å per minute. An 80 Oe field was applied in the plane of the film during deposition and cooling of the film.

Sputter etching was performed by using a film as a target in an r.f. sputtering system of the J-arm configuration. Power densities of nominally 7 watts/cm^2 for one minute removed about 100Å of film. A 10 Oe field was applied in the plane of the film for the purpose of either maintaining or rotating the anisotropy axis.

Two films were made by r.f. bias sputtering from a 81.5-18.5 Ni-Fe target in 35μ of Argon at a deposition rate of 200Å per minute in an orienting field of 6 Oe. Target to substrate voltage ratios of 3:1 were required to obtain values of H_c and H_k similar to the evaporated films.

The coercive force was measured on a 60Hz B-H looper and H_k by using the method of Beam and Siegle[4] with magnetization 45° to the easy axis. Magnetostriction was measured by noting the change in H_k when the substrate was bent to produce a strain in the film. All of the measurements were made at room temperature. The strain normally used was $5 \cdot 10^{-4}$ and all of the evaporated films had magnetostriction, η, of less than 10^3. Typical values of H_k and H_c were 3.5 and 2.0 Oe.

Results

Curves of ΔH_c vs. time and $\Delta\eta$ vs. time, at constant temperature, are shown in Figure 1. The shape of these curves usually shows a rapid approximately logarithmic change followed by a slower linear change; however, this sequence is not always true. The response of an evaporated NiFe film to several days of aging at 127°C is shown in Figure 1a. Details of the initial response period of two bias sputtered Ni-Fe films aged at 225°C are shown in Figure 1b where a substrate influence is evident. Each of the three films was aged in air with a bias field applied along the easy axis.

4. Beam, W. R., and Siegle, W. T., Rev. Sci. Instrum, 36, 641 (1965).

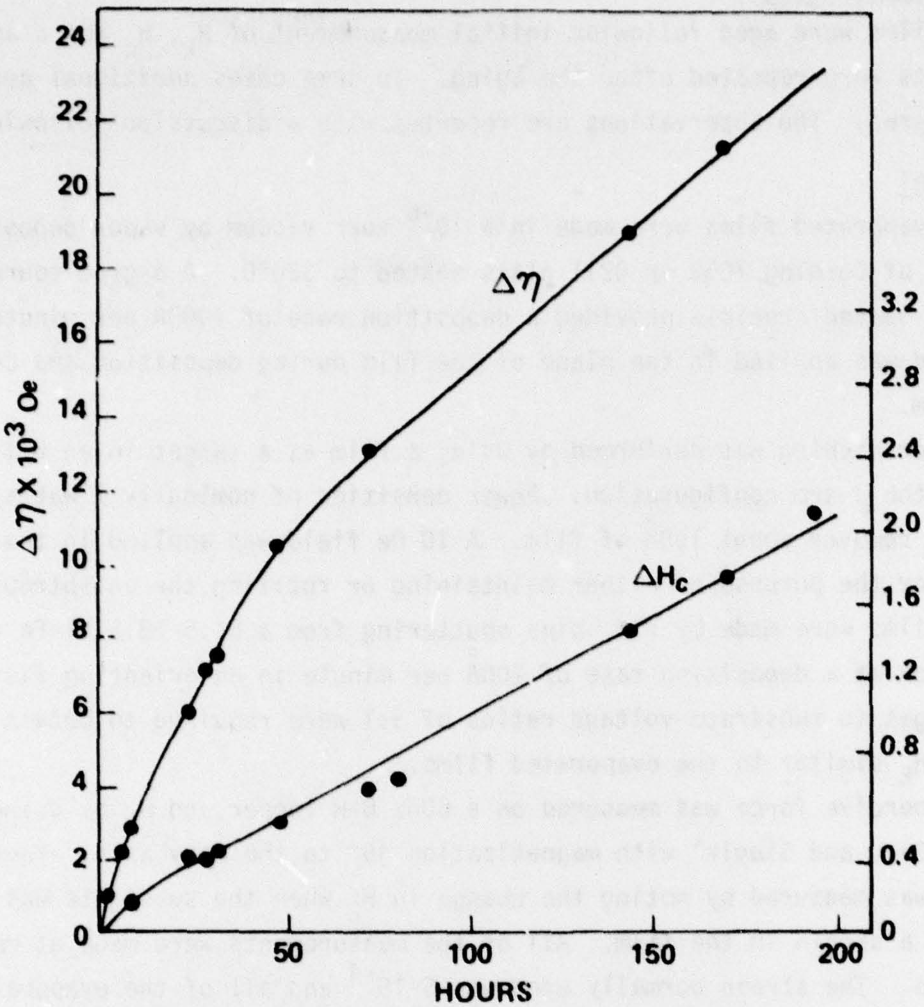

FIG. 1a EVAPORATED Ni-Fe AGED AT 127°C

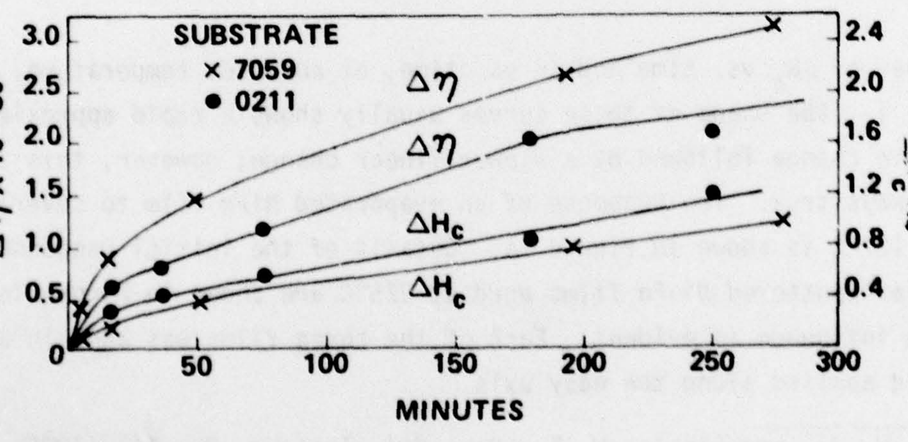

FIG. 1b BIAS SPUTTERED Ni-Fe AGED AT 225°C

Figure 1. Magnetostriction and Coercive Force Responses to Aging

Binary NiFe films, regardless of preparation method or subsequent treatment, show an average reduction of 10% in H_k when the films are stored for 3 days in air at 150°C with a bias field parallel to the easy axis. Similar treatment of Ni-Fe-Au films bearing 12wt % gold show only a ±6% change in H_k in 6 months. All films including the ternary gold composition (Figure 2) show large changes in H_k, due to magnetic annealing, when the bias field is positioned normal to the easy axis. However, high substrate temperature during deposition and particularly high temperature vacuum annealing following deposition reduce the rate of change.

The time required for a 1 Oe change in H_c at various temperatures is shown in Figure 3. Similarly shaped curves in Figure 4 show the time required for a given change in η is as much as three orders of magnitude greater for the 19% Au film, the bias sputtered film and the sputter etched Ni-Fe film compared to the evaporated Ni-Fe film on 0211 glass. The figure suggests the time difference would have been even greater if a common value of η had been available for all of the films. Additional measurements, not shown in the figure, indicate evaporated Ni-Fe films on 0211 glass age about an order of magnitude faster than those on 7059 glass. This substrate effect was less evident in bias sputtered films. Extrapolation towards lower temperature of the Ni-Fe-Au curve of Figure 4 resulted in good agreement with the averaged response of six Au bearing films aged at low temperature.

Evaporated Ni-Fe films with additions other than gold were tested at 150°C. Films made from a melt with 10% Pd or 5% Pd and 3% Co added to the Ni-Fe had magnetostriction changes six times those for a Ni-Fe-Au film after 8 months at 150°C. Addition of 10% Si to the Ni-Fe melt produced a magnetostriction change 25 times that for Ni-Fe-Au films. The addition of 7% Co to the Ni-Fe melt decreased the rate of magnetostriction change with respect to that of evaporated Ni-Fe, but the change was still more rapid than that of the Ni-Fe-Au and the bias sputtered films.

When dispersion, skew and magnetoresistance coefficient $\Delta R/R$ were measured the following emerged. The dispersion, skew and magnetoresistance were smaller in Ni-Fe-Au films than in evaporated Ni-Fe.[5] Magnetoresistance in 350Å evaporated films measured 1.6% in the ternary and 2.2% in the binary composition. Sputter

5. Irons, H. R., Czech. J. Phys. B21, 500 (1971).

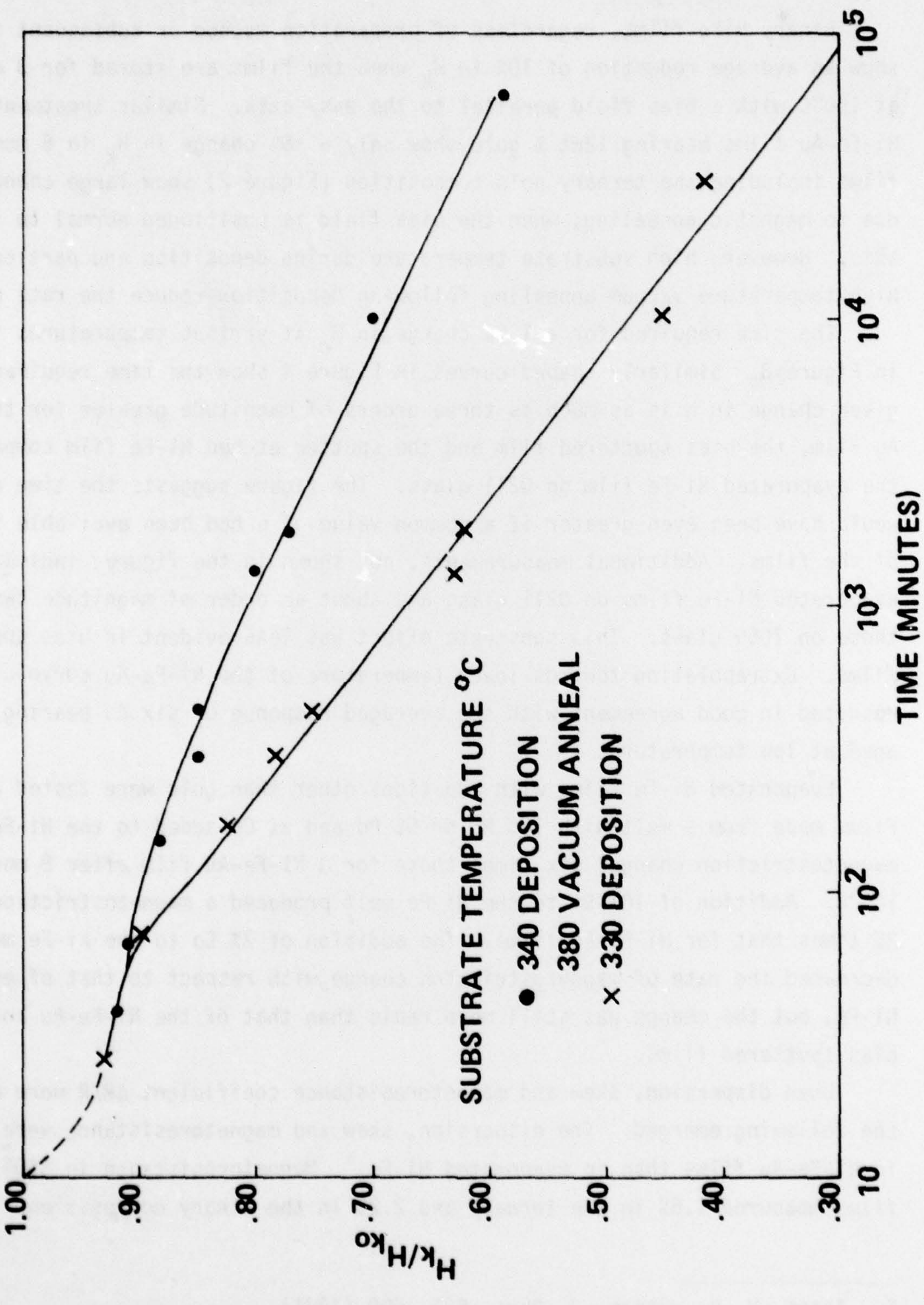

Figure 2. Deterioration of H_k in a Saturating Hard Axis Field at 150°C in Air

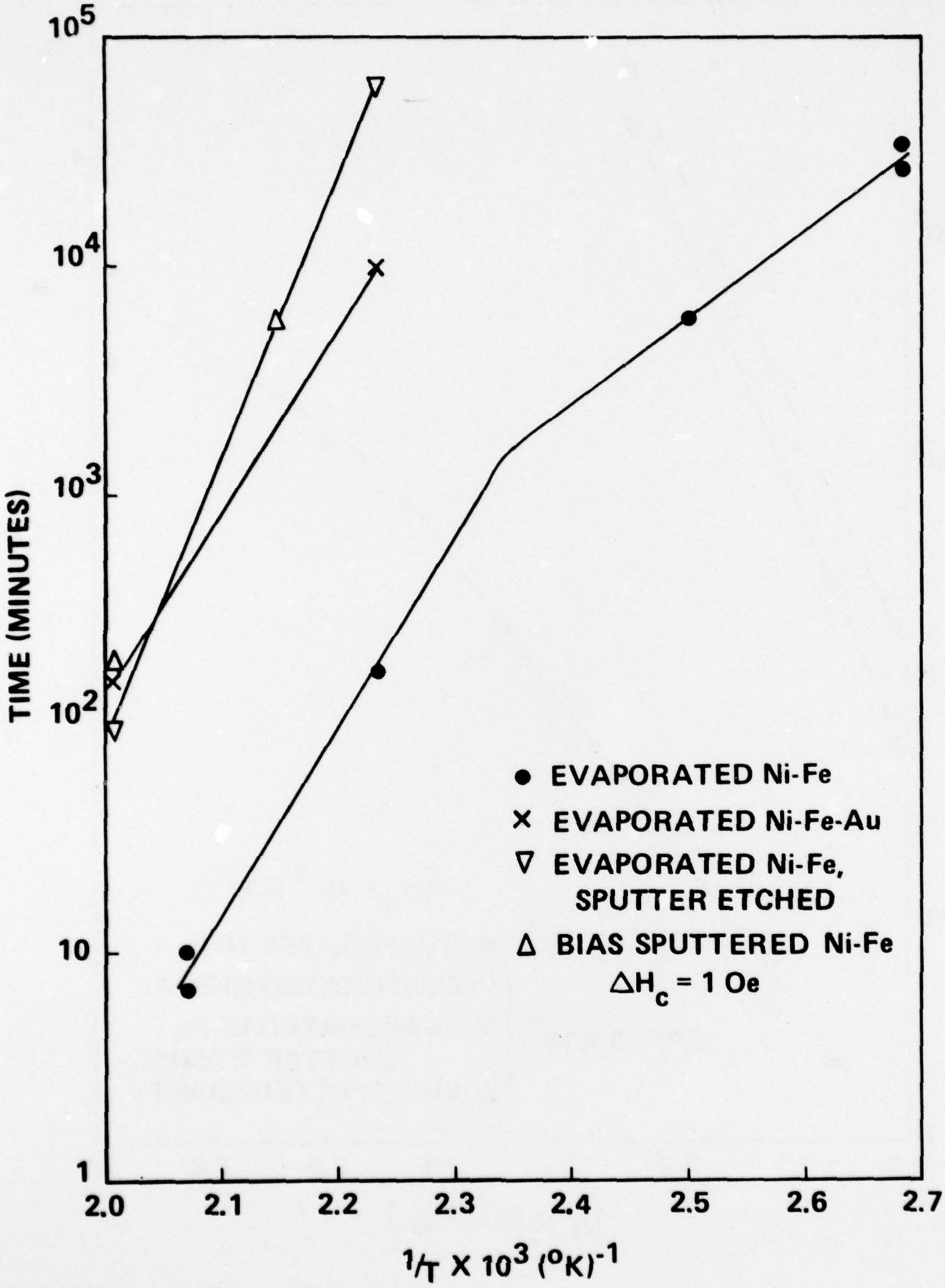

Figure 3. Incremental Change in H_c as a Function of Time and Temperature

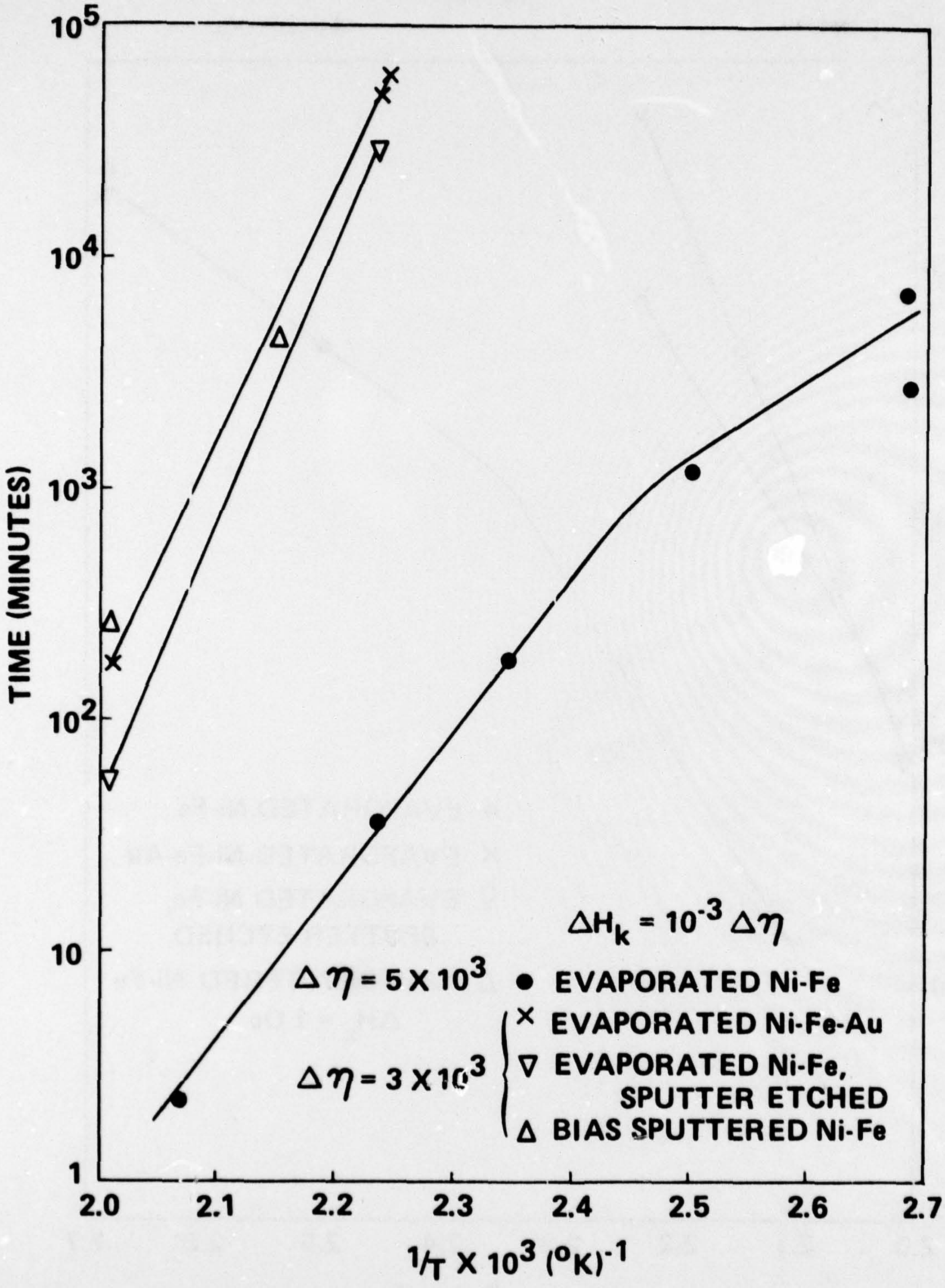

Figure 4. Incremental Change in η as a Function of Time and Temperature

etching of the evaporated Ni-Fe did not reduce the nominally 2% $\Delta R/R$. A nominal ratio of 1% was observed in the bias sputtered Ni-Fe films. The bias sputtered result might be improved by modified technique.

An interesting observation during the sputter etching experiments was the rapid rotation, in a few minutes, of the anisotropy axis into alignment with an applied field. The orientation of the original anisotropy was 90° to the applied field and the value of the rotated anisotropy in some cases nearly equalled the original value. Thermal effects were ruled out by shielding a part of several films with thin glass substrates. Areas protected from the plasma evidenced neither rotation nor degredation of the original anisotropy.

Evaporated films were essentially free of magnetostriction as deposited but consistently developed magnetostriction under sputter etching, usually indicative of a composition excessive in Fe. In no case was the composition more than a few tenths weight per cent from the zero magnetostriction composition (ZMC). Likewise the bias sputtered films were a few tenths per cent off ZMC; consistently Ni rich.

Discussion

The oxidation of an evaporated Ni-Fe film 200Å thick for 50 hrs at 250°C is reported to increase the H_c to 75 Oe.[3] This increase is considerably larger than the value of 22 Oe observed in our measurements for a 300 hr treatment at 225°C on a 250Å thick evaporated film. The 300 hrs at 225°C is equivalent to 50 hrs at 250°C for the data shown in Figure 3. The difference in the two values of H_c may be due to the different film thickness or the data of Figure 3 may not apply for large increases in H_c.

The large change in magnetostriction due to oxidation is understandable from the data of Pollak and Bajorek[6] on film composition vs thickness for an evaporated Ni-Fe film that had been in air at room temperature for three weeks.

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3. Gangulee, A. et al, IEEE Trans. Magn. MAG-10, 848 (1974).
6. Pollak, R. A., and Bajorek, C. H., J. Appl. Phys. 46, 1382 (1975).

The data show a surface oxide layer 12Å thick which is rich in iron oxide and low in nickel oxide. A 12Å layer under the oxide is deficient in Fe and high in Ni compared to the remainder of the film. This depletion in iron is apparently due to migration across the oxide boundary, and the change in magnetostriction observed as the film is oxidized reflects that depletion. The thin oxide layer in permalloy is probably formed very rapidly since Kruger and Yolken[7] have shown that pure iron forms an oxide layer 20Å thick in 15 minutes at room temperature.

Lawless has indicated that structural defects in the surface oxide layer and ionic mobility in the metal play an important part in the oxidation process[8]. Both the structure of the NiFe surface[6] and observed rotation of H_k are evidence of appreciable reordering. If these effects were dominated by the same dynamic mechanisms, such as the vancies of Takayasu[1], similarities in activation energy should be evident. The analytical method of Takayasu was applied to the data of Figure 3 for examination of this premise.

Figure 3 indicates only evaporated NiFe films responded with a change in H_c to aging in air below 125°C. The activation energy for these films was 0.75ev. This energy is very close to 0.85ev reported by Takayasu for the excess vacancy first stage of annealing in vacuum. However, the observed frequency factor, $10^4 sec^{-1}$, associated with this aging is in poor agreement with the frequency factor, $10^7 sec^{-1}$, reported for vacuum annealing.

Sputtered, sputter etched and gold bearing evaporated films aged at temperatures above 150°C evidenced an activation energy of 2ev. This energy is in good agreement with the 2.2ev reported for the second stage of vacuum annealing which occurs through equilibrium vacancy dynamics. But again, the observed frequency factor, 10^{16} sec^{-1}, does not agree well with the vacuum annealing value of $10^{14} sec^{-1}$.

Oxidation is a more complex phenomena than the vacuum annealing to which the Takayasu theory is directly applicable so dissimilar frequency factors are not surprising. The concurrent similarities in activation energy are quite

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1. Takayasu, M. et al, IEEE Trans. Magn. MAG-10, 552 (1974).
6. Pollak, R. A., and Bajorek, C. H., J. Appl. Phys. 46, 1382 (1975).
7. Kruger, J., and Yolken, H. T., Corrosion 2, 20 (1964).
8. Lawless, K. R., Reports on Progress in Phys. 37 (2), 231 (1974).

interesting in that the value for each of the types of films investigated compares well with that for one of the stages of vacuum annealing. The similarities suggest high excess vacancy concentration in the evaporated Ni-Fe films and near equilibrium concentration in the other films.

The very low oxidation rate for bias sputtered and sputter etched films is of considerable practical interest. Two possible reasons for the low rate are offered: either the vacancy concentrations are altered as discussed above with a consequent decrease in oxidation dynamics or ion bombardment creates a barrier against oxygen penetration. The latter might occur through a direct effect on the diffusion constants from Argon trapped within the lattice or modification of the film surface microstructure, by the large energy dissipation associated with ion bombardment, may result in a surface structure easily passivated upon air exposure.

The relationship between vacancy dynamics, vacancy concentration and ion bombardment ($\leq$ 900 ev) is not known. However, the rapid rotation of the anisotropy when a film is sputter etched in a field normal to the easy axis suggests that the vacancies are in great excess or are very mobile during ion bombardment. But it is also observed the magnitude of H_k seldom returns to the original value following rotation.

By definition vacancies occur in a surface being sputtered and can be expected well in excess of thermal equilibrium at least near the surface. The film thicknesses and ion energies used here probably allow ion penetration about halfway through the films but if the not implausible assumption of full film penetration is accepted each "e" region of the Takayasu theory is affected and the experimental situation accommodates the first stage theory fairly well. The theory allows a large portion of but not the total anisotropy to derive from first stage annealing; a prediction that correlates with the experimental result of normally less than full recovery of the magnitude of H_k. Less than full film penetration by the incident ions leads to the same result through exclusion of some "e" regions from contributing. However, no well defined dependence of rotation on either ion energy or film thickness has been noticed. The experimental effort to date is not sufficient for conclusive comments on these parameters.

Further assessment of the adequacy of this excess vacancy model is considerably complicated by the difficulty in comparing the dynamics of the thermally driven system with that of the ion driven system. While the fast rotation of H_k in the ion driven system is not difficult to accept, similarly rapid thermalization of the excess vacancies following ion bombardment seems necessary to maintain application of the Takayasu theory in view of the observed resistance of the ion bombarded films to oxidation. Recall, the activation energy of these films aging in air correlates well with that for a second stage process involving only equilibrium vacancies.

Allowing highly mobile vacancy dynamics under ion bombardment, retaining the Takayasu framework and assuming the original vacancy concentration of the film to be stable, except at the eroding surface of course, is not entirely consistent with the results either. Certainly enough energy is provided to activate the second stage process for rotation of the anisotropy; that it can be distributed among the various "e" regions is less certain but plausible. Stability against oxidation is indicative of equilibrium vacancy concentration so the sputtered and gold bearing film results are consistent with the assumptions here. However, it is observed that the evaporated NiFe films, which appear to have an appreciable excess vacancy concentration prior to ion bombardment demonstrate aging characteristics typical of equilibrium vacancy concentration following ion bombardment thereby violating an initial assumption.

Reorientation of H_k indicates an atomic reorientation occurs within these films under ion bombardment. The features of the Takayasu theory simply may not apply to ion bombardment in which case the inconsistencies described would be moot, but much of the experimental result is consistent with the theory and the correlations of activation energy are quite suggestive. Further experimentations with a wider variety of film thicknesses and other variations should clarify the mechanisms. Additional effort appears justified by the results to date.

While even the easily oxidized evaporated Ni-Fe films can be protected from oxidizing by an appropriate coating, the change in magnitude of H_k due to annealing with a bias field normal to the easy axis (Figure 2) cannot be prevented by such a technique in any of the films. The annealing could be troublesome in many applications and only the rate can be affected. Taylor reported a 1.2° change

in the direction of the easy axis of a film stored at room temperature for 10^4 hours with a bias field 45° to the easy axis.[9]

9. Taylor, C. F. et al, J. Appl. Phys. 42, 1755 (1971).

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2. Fujii, T. et al, IEEE Trans. Magn. MAG-4, 515 (1968).
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7. Kruger, J., and Yolken, H. T., Corrosion 2, 20 (1964).
8. Lawless, K. R., Reports on Progress in Phys. 37 (2), 231 (1974).
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